

# FACTORS AFFECTING THE LEACHING OF NITROGEN SPECIES FROM DIATOMACEOUS MUDSTONE

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## Abstract

Horonobe Underground Research Center, located in northern Hokkaido, Japan, has been excavating shafts and drifts of an underground research facility to establish general techniques for the assessment of deep geological environment. In this site, the groundwater seepage from the shafts and drifts as well as leachate from the excavated rock storage site contains high concentrations of total nitrogen. Ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ), the major nitrogen species in the seepage and leachate, has been removed by a nearby treatment facility. However,  $\text{NH}_4\text{-N}$  is easily oxidized to nitrite-nitrogen ( $\text{NO}_2\text{-N}$ ) and nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) by nitrification in the excavated rock storage site, which makes the removal process employed on site less effective. Therefore, column experiments that simulated the infiltration of rainwater through the storage site were carried out to understand the leaching and nitrification of nitrogen species and the factors affecting the phenomena. The results showed that the nitrification was inhibited when the rock layer was almost saturated, and that this process was temperature dependent. These indicate that nitrification can be mitigated by controlling hydrological conditions like water saturation.

**Keywords:** Column Experiment, Diatomaceous Mudstone, Nitrification, Nitrogen Removal

## Introduction

Horonobe Underground Research Center, located in northern Hokkaido, Japan, has been excavating shafts and drifts of an underground research facility for research and development of general techniques regarding high-level radioactive waste disposal. Currently, the shafts were excavated up to about 350 m [1]. Geological formation of this area is composed of diatomaceous and siliceous mudstone. Groundwater seepage from the shafts and drifts as well as leachate from the waste rock storage site contains high concentrations of total-nitrogen (T-N). The major nitrogen species is ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ) originating from the remains of diatoms. The  $\text{NH}_4\text{-N}$  has been removed by the water treatment facility [2]. However, the  $\text{NH}_4\text{-N}$  is easily oxidized to nitrite-nitrogen ( $\text{NO}_2\text{-N}$ ) and nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) by nitrification in the waste rock storage site [3]. Once the  $\text{NH}_4\text{-N}$  changes to  $\text{NO}_2\text{-N}$  or  $\text{NO}_3\text{-N}$ , the removal of nitrogen species by the facility may become inefficient. In addition, the amount of the rocks is estimated to increase in accordance with excavation of the shafts and drifts [4].

Therefore, column experiments that simulated the infiltration of rainwater through the storage site were conducted to understand the factors affecting the leaching behavior of

nitrogen species and nitrification and to propose countermeasures for restricting nitrification processes.

## Nitrogen Transformations

Figure 1 illustrates the major processes of nitrogen transformations in the waste rock storage site. After  $\text{NH}_4\text{-N}$  is leached from organic nitrogen (Org-N) contained in the remains of diatoms,  $\text{NH}_4\text{-N}$  is oxidized to  $\text{NO}_2\text{-N}$ , which is a rather unstable species in the presence of oxygen and autotrophic ammonium-oxidizing bacteria (the major genera are *Nitrosomonas*). After this first nitrification step, the autotrophic nitrite-oxidizing bacteria (the major genera are *Nitrobacter*) oxidize  $\text{NO}_2\text{-N}$  to  $\text{NO}_3\text{-N}$ . Nitrate-nitrogen is the stable end product of the nitrification processes. Below the groundwater table or in anoxic conditions, the heterotrophic bacteria (the major genera are *Pseudomonas*) reduce  $\text{NO}_3\text{-N}$  to nitrogen gas ( $\text{N}_2$  gas) by denitrification [5].

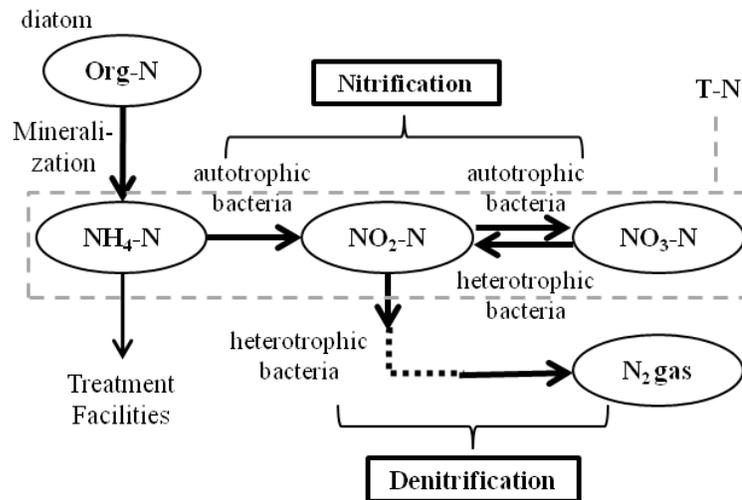


Figure 1. Nitrogen transformations

## Materials and Methods

Rock samples excavated around 140 m below the ground surface were used in the column experiments. The columns were made of acrylic with 5.2 cm in diameter and 30 cm in height. The rock samples were crushed into less than 2 mm in diameter, and 300 g were packed into the columns of 20 cm in height ( $0.706 \text{ g/cm}^3$  in bulk density). Figure 2 (a) shows a schematic of the column filled with the samples. The columns were set in the laboratory at controlled temperature ( $25^\circ\text{C}$ ).

To simulate the actual infiltration of rainwater through the storage site, 60 mL deionized water was sprinkled into the columns using a rainfall simulator once a week. After 3 days, the effluents were collected using PE bottles set under the columns. The pH, electrical conductivity (EC), oxidation-reduction potential (ORP), temperature, and concentrations of dissolved oxygen (DO) of the effluents were measured, followed by filtration of the effluents using  $0.22 \mu\text{m}$  membrane filters for the analysis of the concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and coexisting ions by ion chromatography. Concentrations of total organic carbon and alkalinity of the effluent were also measured.

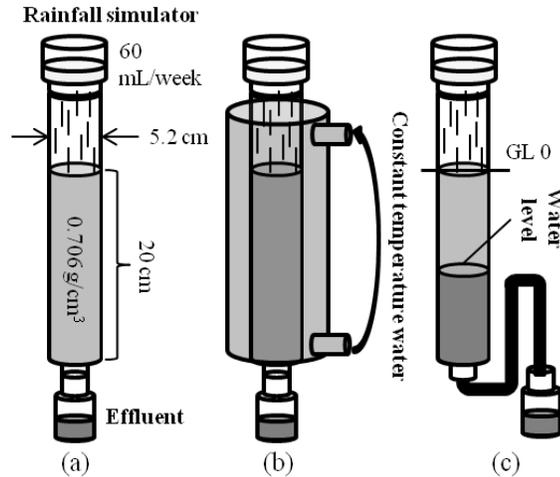


Figure 2. Schematics of the column experiments

To understand the factors affecting leaching behavior of nitrogen species, six columns were constructed as listed in Table 1.

The effect of the salinity of pore water was examined since the seepage from the shafts and drifts contains chloride ion ( $\text{Cl}^-$ ) concentration of 3500 mg/L [6]. Sodium chloride was added to deionized water for simulating groundwater as shown in case 2 to examine the effect of the salinity of pore water at room temperature.

It is important to investigate the effect of temperature and oxygen concentration on nitrification [7]. A circulation system of constant-temperature water as shown in Figure 2 (b) was used in cases 3 and 4 to adjust the temperature at 35 and 15 °C, respectively. Water level was adjusted as shown in Figure 2 (c) for the partly-saturated and fully-saturated cases (cases 5 and 6) to examine the effect of water content, or oxygen concentration.

**Table 1. Cases of Column Experiments**

case	$\text{Cl}^-$ concentration	temperature	water saturation	column type
1	0	25 °C	unsaturated	(a)
2	1000 mg/L	25 °C	unsaturated	(a)
3	0	35 °C	unsaturated	(b)
4	0	15 °C	unsaturated	(b)
5	0	25 °C	partly-saturated	(c)
6	0	25 °C	fully-saturated	(c)

## Results and Discussion

Figure 3 shows the change of nitrogen species concentrations in the effluent in case 1. The major nitrogen species were changed from  $\text{NH}_4\text{-N}$  to  $\text{NO}_2\text{-N}$ , and then from  $\text{NO}_2\text{-N}$  to  $\text{NO}_3\text{-N}$  with time. This indicates that the sequential nitrification processes occur.

Figure 4 shows the changes of nitrogen species concentrations in the effluent with different salinity of pore water in case 2. Compared with case 1,  $\text{NH}_4\text{-N}$  concentration was higher since  $\text{NH}_4^+$  was exchanged with  $\text{Na}^+$  contained in the salt water, and  $\text{NO}_3\text{-N}$  concentration was lower because nitrification was somewhat restricted by high salinity condition [8].

Figures 5 and 6 show the changes of nitrogen species concentrations in the effluents at 35 and 15 °C, respectively. Compared with Figure 3 (25 °C),  $\text{NO}_3\text{-N}$  concentration, the end product of nitrification processes, was lower at both 35 and 15 °C, and no  $\text{NO}_2\text{-N}$  was observed at 35 °C. This could be attributed to the susceptibility of autotrophic ammonium-oxidizing and nitrite-oxidizing bacteria to temperature [9]. Specifically, the optimal temperature of these bacteria in northern regions is reported to be 20-25 °C [8]. Since the temperature in summer increases to 20 °C on average in Horonobe, the similar leaching may occur in the waste rock storage site. In contrast, these bacteria are inactive at lower temperature.

Figures 7 and 8 show the changes of nitrogen species concentrations in the effluents under partly-saturated and fully-saturated conditions, respectively. Under fully-saturated condition (Figure 8, case 6),  $\text{NO}_3\text{-N}$  was not detected except around 40 days. This indicates that nitrification can be mitigated by controlling the water level. However, under partly-saturated condition (Figure 7, case 5), nitrification took place.

From the above results, controlling the temperature and water level is effective in restricting the nitrification. Therefore, the “immersing method” as an example of in situ countermeasures for restricting nitrification processes is effective, as illustrated in Figure 9. Applying this method to the waste rock storage site could control nitrification, resulting in a decrease in  $\text{NO}_3\text{-N}$  concentration.

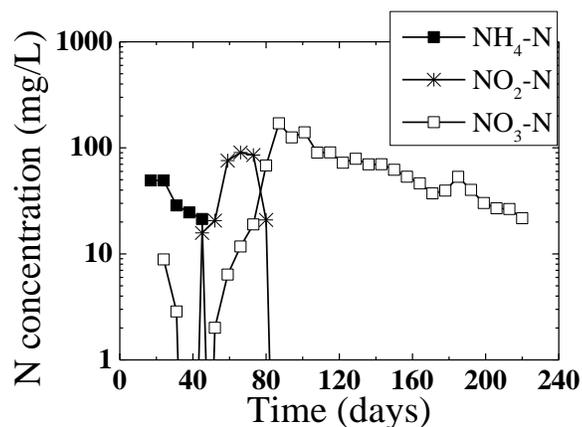


Figure 3. Nitrogen species concentration changes in case 1

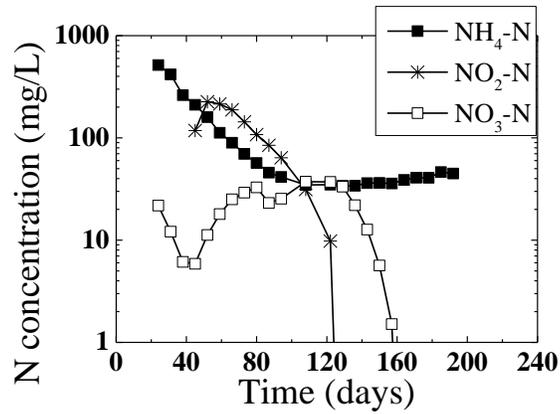


Figure 4. Nitrogen species concentration changes in case 2 (high salinity)

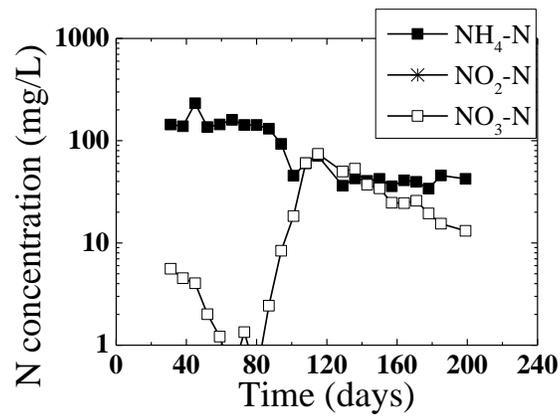


Figure 5. Nitrogen species concentration changes in case 3 (35 °C)

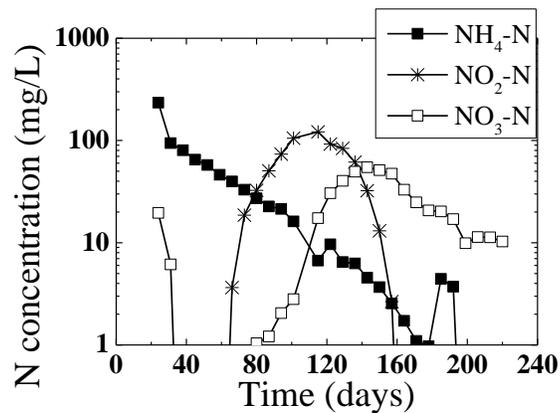


Figure 6. Nitrogen species concentration changes in case 4 (15 °C)

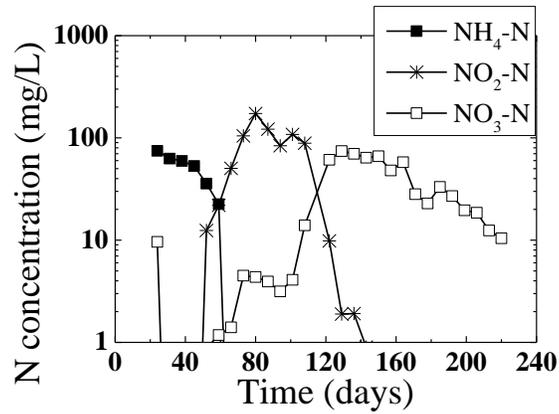


Figure 7. Nitrogen species concentration changes in case 5 (partly-saturated)

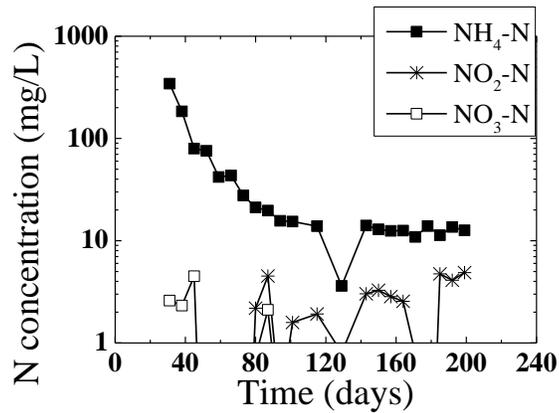


Figure 8. Nitrogen species concentration changes in case 6 (fully-saturated)

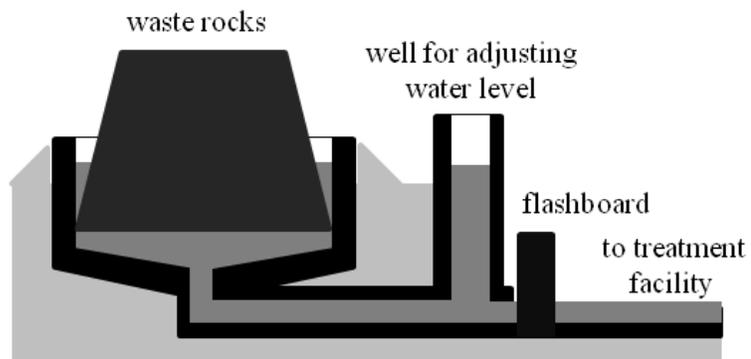


Figure 9. Schematic of the immersing method

## Conclusions

Nitrification of  $\text{NH}_4\text{-N}$  in the leachate from the storage site of diatomaceous mudstone was restricted under saturated condition. The in situ flooding method in summer could provide an effective countermeasure to prevent nitrification. However, quantitative evaluation of factors affecting the leaching behavior of nitrogen species and nitrification should be required.

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